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SPECTROGRAPHIC SOLUTION ANALYSIS OF ALUMINUM ALLOYS

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ABSTRACT

To obtain accurate analyses of metals and alloys with the most widely used technique of spectrographic analysis, i.e., the point-to-plane spark technique, the standards and the unknown material must be quite similar in size, shape, chemical composition, and metallurgical state. By dissolving the sample and using the vacuum cup spark technique to analyze the solution, these limitations can be circumvented. Standards can be synthesized easily by mixing aliquots of master reference solutions. The solution technique also offers the possibility of adding an internal standard and, thereby, obtaining a wider selection of reference lines to use in the analysis.

The solution spectrographic method has been investigated and applied to a wide variety of analytical problems at this Center. As an example, the procedure for the determination of manganese, zirconium, magnesium, vanadium, titanium, and iron in types 2219 and 2319 aluminum alloy is presented. The results agree with the results of classical wet methods and are precise to $\pm 0.005\%$ in the concentration ranges involved.

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SUMMARY

To obtain accurate analyses of metals and alloys with the most widely used technique of spectrographic analysis, i. e., the point-to-plane spark technique, the standards and the unknown material must be quite similar in size, shape, chemical composition, and metallurgical state. By dissolving the sample and using the vacuum cup spark technique to analyze the solution, these limitations can be circumvented. Standards can be synthesized easily by mixing aliquots of master reference solutions. The solution technique also offers the possibility of adding an internal standard and, thereby, obtaining a wider selection of reference lines to use in the analysis.

The solution spectrographic method has been investigated and applied to a wide variety of analytical problems at this Center. As an example, the procedure for the determination of manganese, zirconium, magnesium, vanadium, titanium, and iron in types 2219 and 2319 aluminum alloy is presented. The results agree with the results of classical wet methods and are precise to ±0.005% in the concentration ranges involved.

INTRODUCTION

Chemical analyses of a wide variety of aluminum alloys are essential in the research and development on materials for space vehicles. The most widely used method for the spectrographic analysis of aluminum alloys is the point-to-plane spark technique, i.e., the sample is made one electrode, and a cone-tipped electrode is the other. A spark to the flat surface of the sample volatilizes some of the material and produces the spectrum. This method has been used at this Center for several years.

To obtain accurate results with the point-to-plane technique, the standards and the unknown must be quite similar in composition, size, shape, and metallurgical state, and both must be free of segregation. Segregation is especially troublesome since only a small amount of sample is actually volatilized. If the size or shape of the sample differs appreciably from the standard, the rates of volatilization of certain elements also differ, and erroneous results may be obtained. Thus, a wide variety of samples requires a large number of standards for analysis. Furthermore, obtaining and/or preparing the necessary standards is often difficult, time consuming, and expensive.

A recent development in the field of spectrographic analysis is the solution method. First, the solid sample is dissolved in an appropriate acid, and the resulting solution then is injected into the spark. Placing the sample in solution eliminates many problems relating to size, shape, metallurgical state, and segregation. Also, to establish working curves, standards of similar composition can be easily and quickly prepared by mixing aliquots from standard solutions of the elements being determined.

In solid samples of aluminum alloys, the aluminum spectrum frequently is used as the internal standard. However, the relative simplicity of the aluminum spectrum severely limits the individual lines which can be used for this purpose. Because of the lack of aluminum lines in the wavelength regions desired, nickel and chromium have been used by personnel of this Center. Another significant advantage of the solution method is that it provides a very wide range of elements which can be selected for use as the internal standard.

Some applications in which the solution method of analysis has been used by this Center include the following determinations: (1) lead in aluminum, (2) silver in aluminum, (3) tin in aluminum, (4) zinc, magnesium, chromium, manganese, titanium, copper, iron, and beryllium in 5000 and 7000 series aluminum alloys, and (5) vanadium, manganese, magnesium iron, zirconium, and titanium in types 2219 and 2319 aluminum alloys. In the first four applications, nickel was used as an internal standard. In the analysis of 2219 and 2319 aluminum alloys, chromium was used as the internal standard. Except for the silver determination, hydrochloric acid followed by nitric acid was used to dissolve the sample. If tin were present, the amount of nitric acid used was held to the minimum required to dissolve the copper. The samples containing silver were dissolved in dilute nitric acid.

Detailed descriptions of all of these analyses are beyond the scope of this report and, therefore, will not be included. A full description of the analysis of 2219 and 2319 aluminum alloys is presented to exemplify the method.

EXPERIMENTAL PROCEDURE FOR 2219 AND 2319 ALUMINUM ALLOYS

Preparation of Master Solutions

a. Copper Master Solution - Dissolve 6.300 grams of electrolytic copper in 50 ml concentrated nitric acid, and dilute the solution to 1 liter.

b. Vanadium Master Solution - Dissolve 0.3571 grams of vanadium pentroxide in 50 ml of 1:1 hydrochloric acid, and dilute the solution to 1 liter.

c. Zirconium Master Solution - Dissolve 0.5299 of zirconium oxychloride octahydrate in 50 ml of 1:1 hydrochloric acid, and dilute the solution to 1 liter.

d. Magnesium Master Solution - Dissolve 0.1658 grams of magnesium oxide in 50 ml of 1:1 hydrochloric acid, and dilute the solution to 1 liter.

e. Iron Master Solution - Dissolve 0.7023 grams of ferrous ammonium sulfate hexahydrate in 50 ml water and 5 ml of concentrated sulfuric acid, and dilute the solution to 100 ml.

f. Titanium Master Solution - Dissolve 0.1668 grams of titanium dioxide in 15 ml of concentrated sulfuric acid and 5 grams of ammonium sulfate, and dilute the solution to 100 ml.

g. Manganese Master Solution - Dissolve 0.9231 grams of manganous sulfate monohydrate in 50 ml of 1:1 hydrochloric acid, and dilute the solution to 1 liter.

h. Chromium Master Solution - Dissolve 49.03 grams of potassium dichromate in water, and dilute to 1 liter.

i. Standard Solutions - At the time this method was developed, no high purity aluminum was available locally; therefore, a sample of aluminum of known composition, Alcoa Standard Aluminum SS1075, was used. Corrections were made for the amounts of various elements present in the aluminum as shown in Table I. The standard solutions were made in the following manner: Weigh three 0.9315 gram $\pm$ 0.1 mg samples of Alcoa aluminum standard SS1075D; add 20 ml of 1:1 hydrochloric acid to each, and warm gently. After the evolution of hydrogen ceases, add 5 ml of concentrated nitric acid, and boil until the copper dissolves. To each of the solutions, add 20 ml of the chromium solution. Standards are prepared by using these solutions and adding aliquots of the master solutions as shown in Table I.

Apparatus

The following equipment was used: Bausch & Lomb Littrow spectrograph, A.R.L. microdensitometer, electrodes (U.C.P. type 6010 with Teflon cup and cone tipped counter electrode), and A.R.L. automatic developing machine.

Spectrographic Procedure

Place 1-1/2 ml of the standard solution in the Teflon cup around the electrode (Plate I), and spark the solution using the conditions shown in Table II. Each of the three standard solutions is run in triplicate.

The plates are processed in an automatic developing machine for 3 minutes at 20°C in Kodak D-19 developer, 30 seconds in 3% acetic acid, and 3 minutes in Kodak rapid fix, washed 3 minutes in running water, and then dried in a stream of warm air.

The transmissions of the line pairs listed in Table III are read, and the intensity ratios are determined by using an emulsion calibration curve that is established with a rotating step sector. The intensity ratio versus percent of element is plotted for each (FIG 1 through 6). (A background correction was made on the zirconium line.) These plots will be used to determine the concentrations for unknown samples of 2219/2319 aluminum alloys.

Analysis of Unknown (Test) Samples of 2219/2319 Aluminum Alloys

Dissolve 1.000 gram of the test alloy in 20 ml of 1:1 hydrochloric acid. After the evolution of hydrogen ceases, add 5 ml of concentrated nitric acid, and heat to dissolve the residue of copper. Add 20 ml of the chromium master solution, transfer to a 100 ml volumetric flask, dilute to the mark, and mix well. Spark 1.5 to 2 ml of the sample solution under the same conditions as the standard solutions. Determine the intensity ratios. The percent of each element is determined from the working curves of intensity ratios versus concentration.*

Accuracy and Precision

Two different samples were analyzed to check precision. Three solutions of each sample were prepared, and each of these solutions was analyzed in triplicate. From the working curves, the amount of each element was determined. The standard deviation and the percent deviation from the average were calculated, and the results are shown in Table IV. The data show that, in analyzing for constituents normally present from 0.1 to 0.2% (by wt) in aluminum alloys, the deviation will range from 2 to 5% of the value determined, i.e., for 0.100% of X, the precision normally is $\pm$0.002 to 0.005%. The apparently high percent deviation of the magnesium analysis is due to the extremely low concentration. Even at this low value, 1.8 ppm, the deviation is only $\pm$0.4 ppm.

With respect to accuracy, analysis of a solution of an aluminum alloy by both the spectrographic and classical wet methods gave the results shown in Table V. The agreement between results was excellent, generally better than 3% of the actual value in the range of 0.1 to 0.4%.

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*Spectrographic methods do not give sufficient accuracy to satisfy the requirements for the determination of copper when it is present at approximately six percent. Therefore, no data for copper are given.

CONCLUSIONS

The solution technique of sample preparation for analysis provides an excellent and rapid method for use with aluminum alloys normally employed in the Saturn program.

Precision of analyses typical alloys 2219/2319 ranged from 2 to 5% (by wt) of the value determined; i.e., for 0.100% X, the result will be precise to $\pm$0.002 to $\pm$0.005%.

Analysis of a sample by both the solution spectrographic and classical wet methods of analysis showed excellent agreement between results (i.e., accuracy), generally better than 3% of the value determined in the range of 0.1 to 0.4% constituent in the alloy. As a general approach to the analyses of aluminum alloys, this method is recommended for use in laboratories where suitable standards are not available or where a large variety of aluminum samples are received, particularly if the spectrographer has little control over the size, shape, and metallurgical condition of the sample. Other internal standards can be used if the sample contains chromium or if chromium interferes. Nickel may be used as an internal standard in the analyses of 5000 and 7000 series alloys.

TABLE I

PREPARATION OF STANDARD SOLUTIONS FOR ANALYSIS OF 2219/2319 ALUMINUM ALLOYS - INTERNAL STANDARD ALIQUOTS

Standard Solution	Element	Milliliters of Master Solution	Grams from Master Solution	Grams from Aluminum Master Solution*	Total Grams	Percent of Total Weight
A	Copper	10.0	.0630	0.00007	0.06307	6.30
	Manganese	10.0	.0030	0.00001	0.00301	0.30
	Vanadium	5.0	.0010	0	0.0010	0.10
	Zirconium	10.0	.0015	0	0.0015	0.15
	Magnesium	1.0	.0001	0	0.0001	0.010
	Titanium	1.5	.0015	0.00005	0.00155	0.155
	Iron	0	0	0.00098	0.00098	0.098
	Silicon	0	0	0.00060	0.00060	0.060
	Aluminum	-	-	0.9298	0.9298	-
B	Copper	8.0	.0504	0.00007	0.05047	5.10
	Manganese	15.0	.0045	0.00001	0.00451	0.46
	Vanadium	2.5	.0005	0	0.0005	0.051
	Zirconium	5.0	.00075	0	0.00075	0.076
	Magnesium	0.5	.00005	0	0.00005	0.0051
	Titanium	1.0	.0010	0.00005	0.00105	0.106
	Iron	1.0	.0010	0.00010	0.00200	0.202
	Silicon	0	0	0.00060	0.00060	0.061
	Aluminum	-	-	0.9298	0.9298	-
C	Copper	12.0	.0756	0.00007	0.07567	7.57
	Manganese	5.0	.0015	0.00001	0.00151	0.151
	Vanadium	10.0	.0020	0	0.0020	0.20
	Zirconium	15.0	.00225	0	0.00225	0.225
	Magnesium	0.2	.00002	0	0.00002	0.002
	Titanium	2.0	.0020	0.00005	0.00205	0.205
	Iron	2.0	.00201	0.00096	0.00297	0.297
	Silicon	0	0	0.00060	0.00060	0.060
	Aluminum	-	-	0.9298	0.9298	-

*Original amounts of each element in solution of alloy before addition of internal standard aliquots.

TABLE II

SPECTROGRAPHIC CONDITIONS FOR ANALYSES OF 2219/2319 ALUMINUM ALLOYS

Excitation	a.c. Spark
Powerstat setting	8
R.F. amperage	6.0 amps
Inductance	100 micro henries
Capacitance	.0050 microfarads
Secondary resistance	0
Discharges per 1/2 cycle	4
Auxiliary gap	4 mm
Analytical gap	3 mm
Exposure	75 seconds
Pre-spark	5 seconds
Spectrograph slit width	20 microns
Source-to-slit distance	14.5 inches
Spectrograph range	2550A° to 3550A°

TABLE III

LINE PAIRS

Reference Line	Internal Standard Line
2924.02 VII	2922.45 Cr
2939.30 Mn	2922.45 Cr
2824.37 Cu I	2922.45 Cr
2795.53 Mg II	2922.45 Cr
2599.40 Fe II	2922.45 Cr
3234.52 Ti II	2922.45 Cr
3273.05 Zr II	2922.45 Cr

TABLE IV

PRECISION

SAMPLE A — SAMPLE I

Element	Average Percent Present*	Standard Deviation	Percent Deviation of Result
Iron	0.195	0.011	4.5
Magnesium	0.0018	0.00044	22.2
Manganese	0.37	0.025	5.1
Titanium	0.125	0.010	4.1
Vanadium	0.106	0.006	3.8
Zirconium	0.097	0.002	1.9

SAMPLE B — SAMPLE II

Element	Average Percent Present*	Standard Deviation	Percent Deviation of Result
Iron	0.143	0.009	3.3
Magnesium	0.00054	0.00012	20.4
Manganese	0.27	0.011	3.7
Titanium	0.214	0.011	4.6
Vanadium	0.098	0.006	5.1
Zirconium	0.165	0.010	5.6

*Triplicate determinations

TABLE V

ACCURACY

Element	Percent Found Chemically	Percent Found Spectrographically	Difference	Percent Difference of Values
Iron	0.146	0.143	0.003	2.0
Manganese	0.260	0.270	0.010	3.7
Iron	0.196	0.195	0.001	0.5
Manganese	0.370	0.370	0.000	0.0

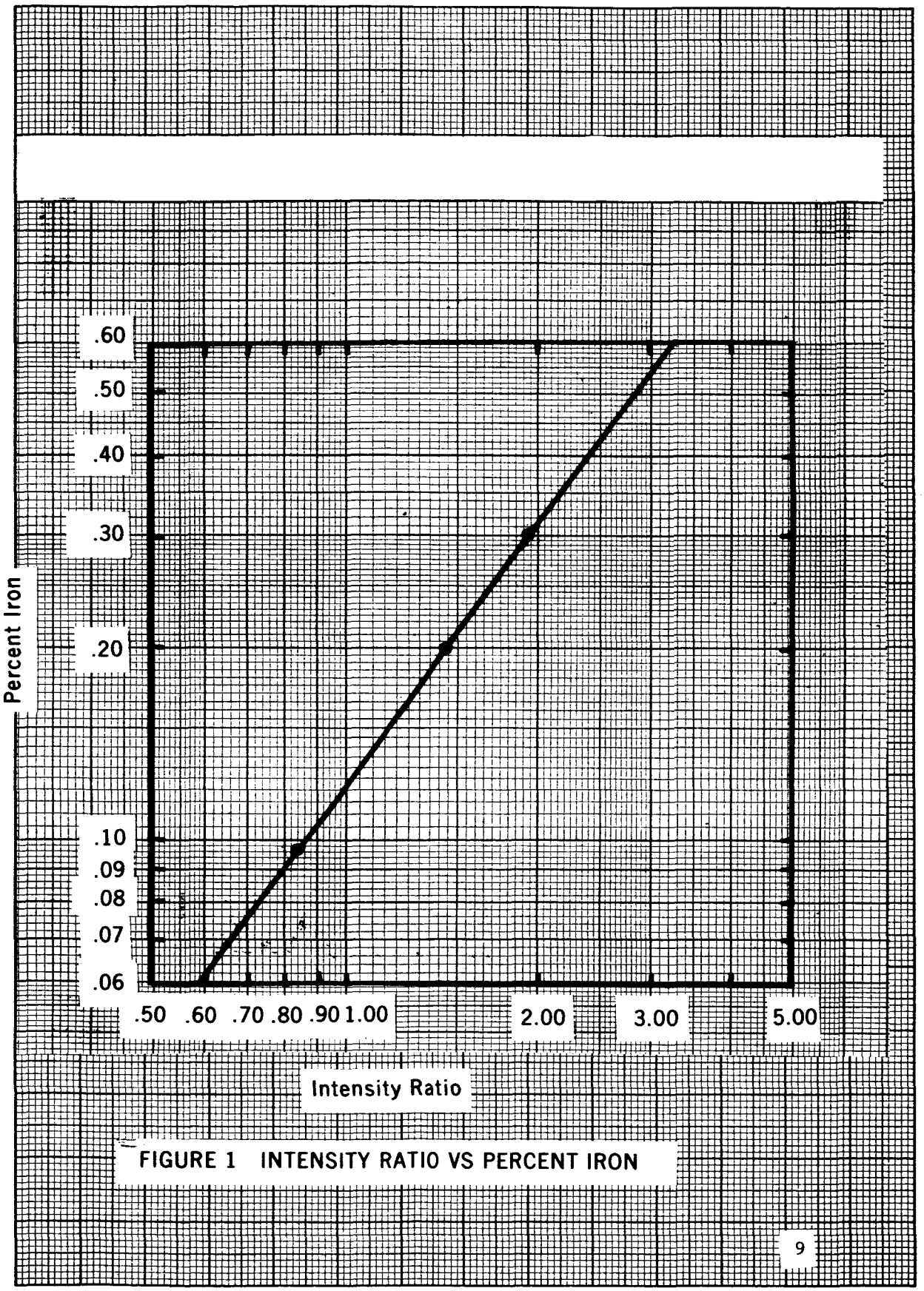

FIGURE 1 INTENSITY RATIO VS PERCENT IRON

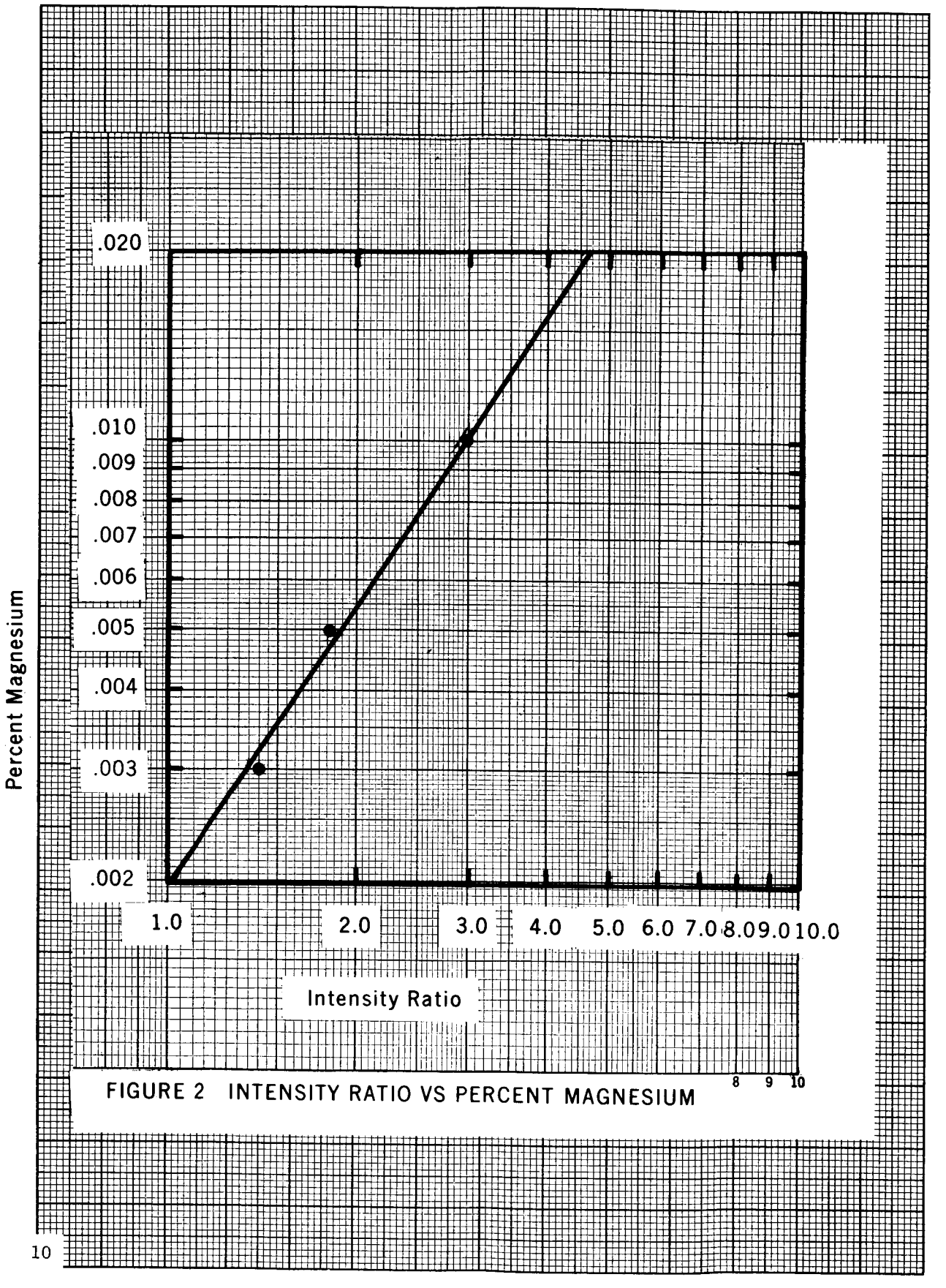

FIGURE 2 INTENSITY RATIO VS PERCENT MAGNESIUM

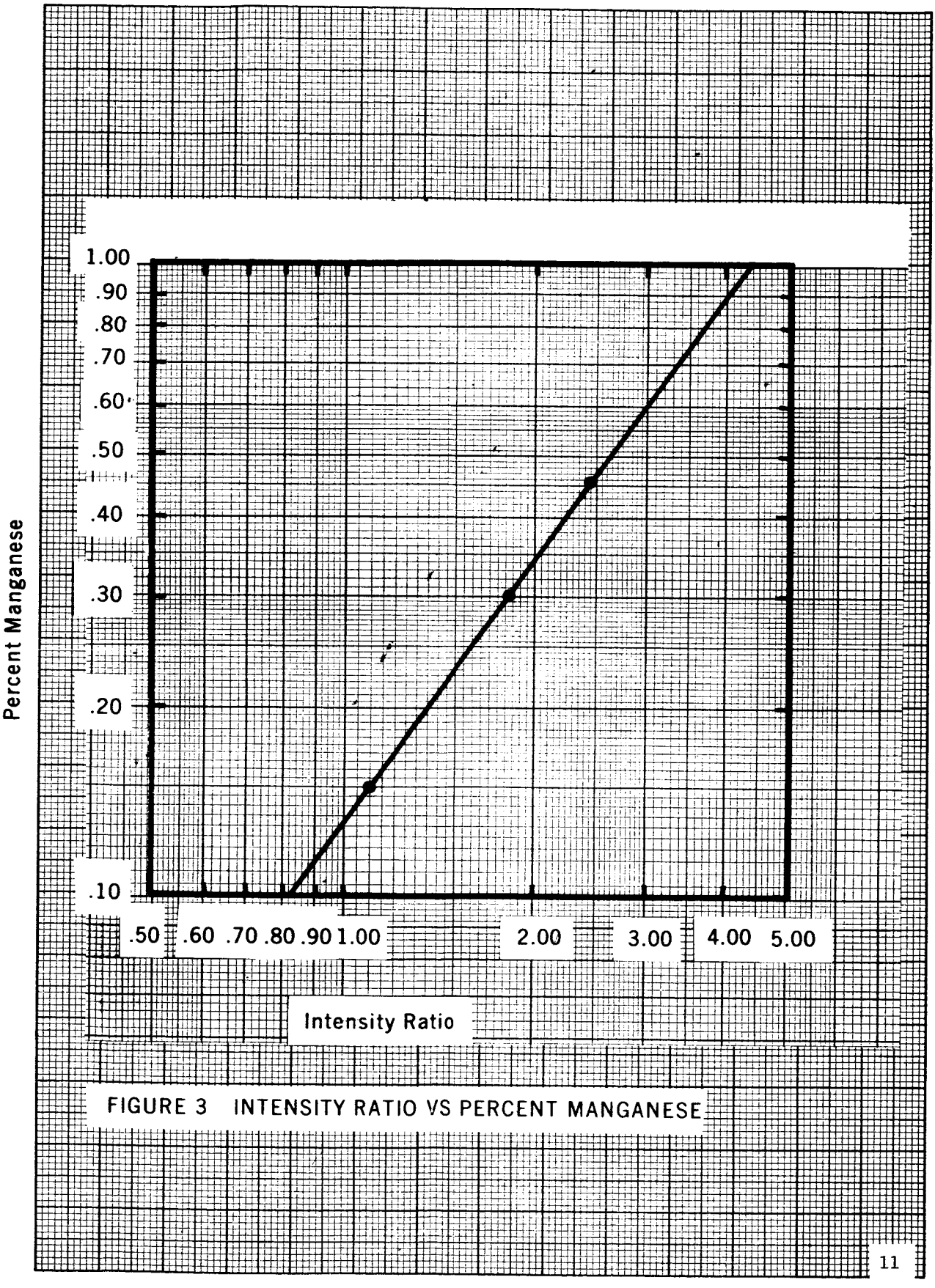

FIGURE 3 INTENSITY RATIO VS PERCENT MANGANESE

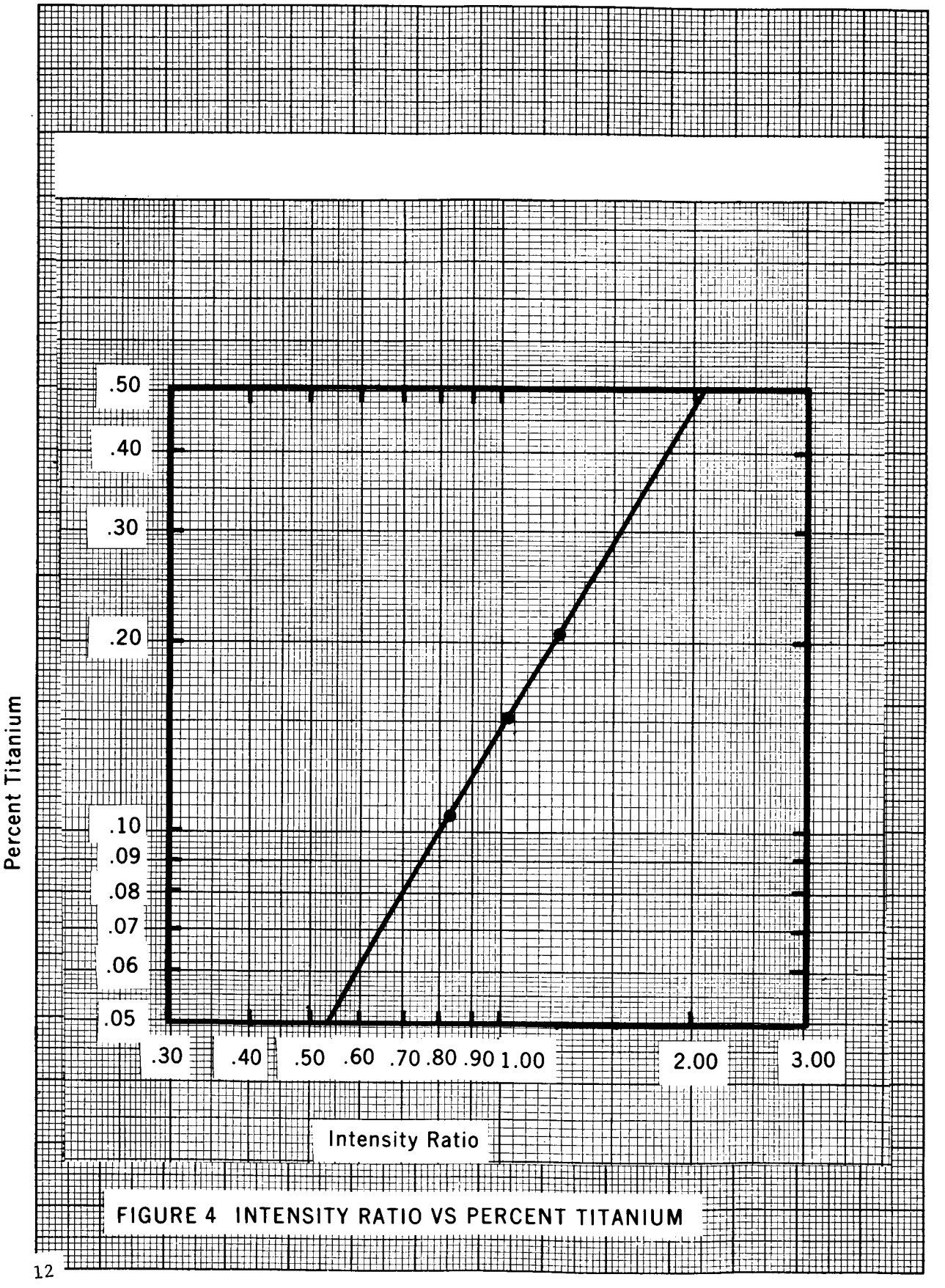

FIGURE 4 INTENSITY RATIO VS PERCENT TITANIUM

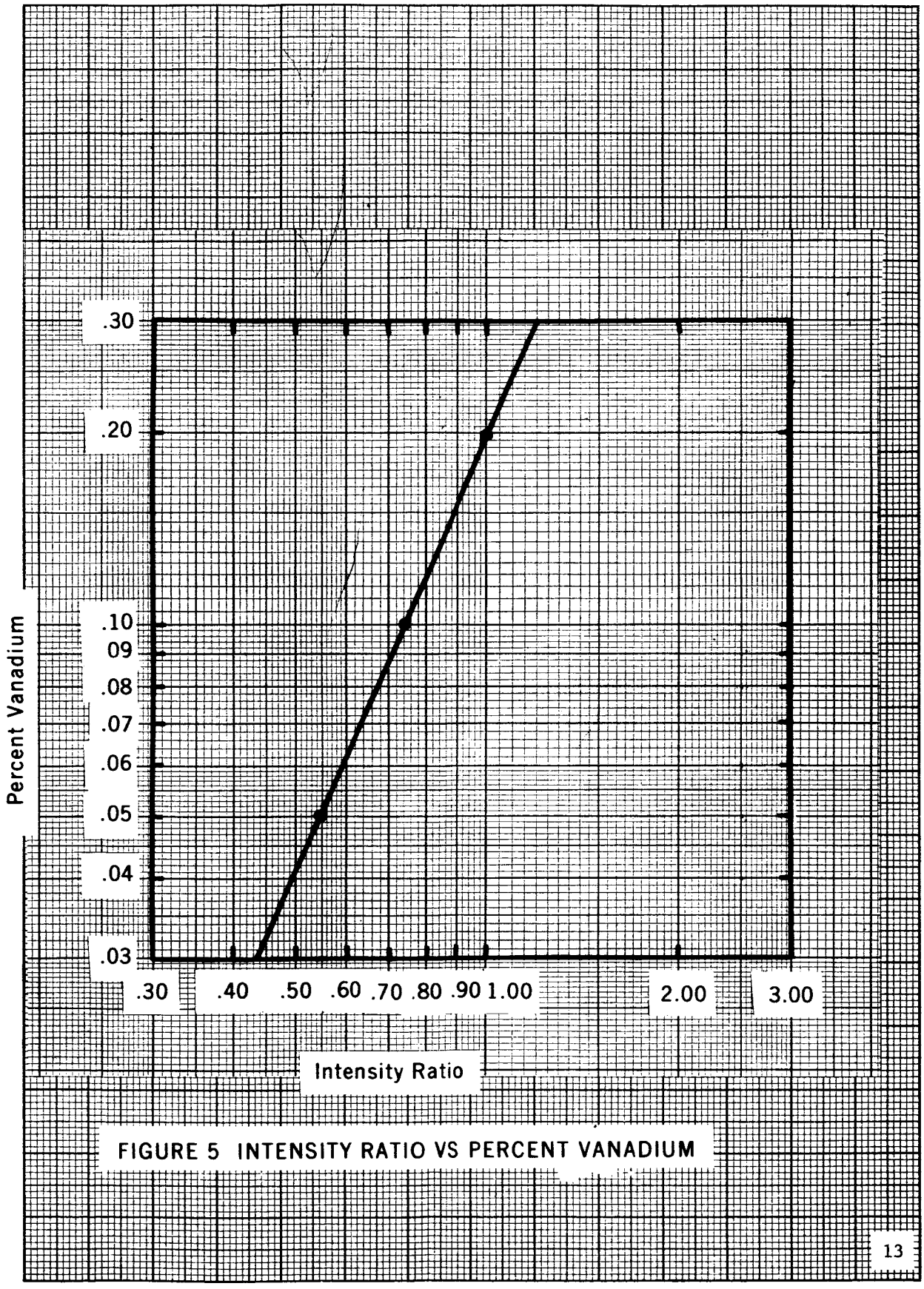

FIGURE 5 INTENSITY RATIO VS PERCENT VANADIUM

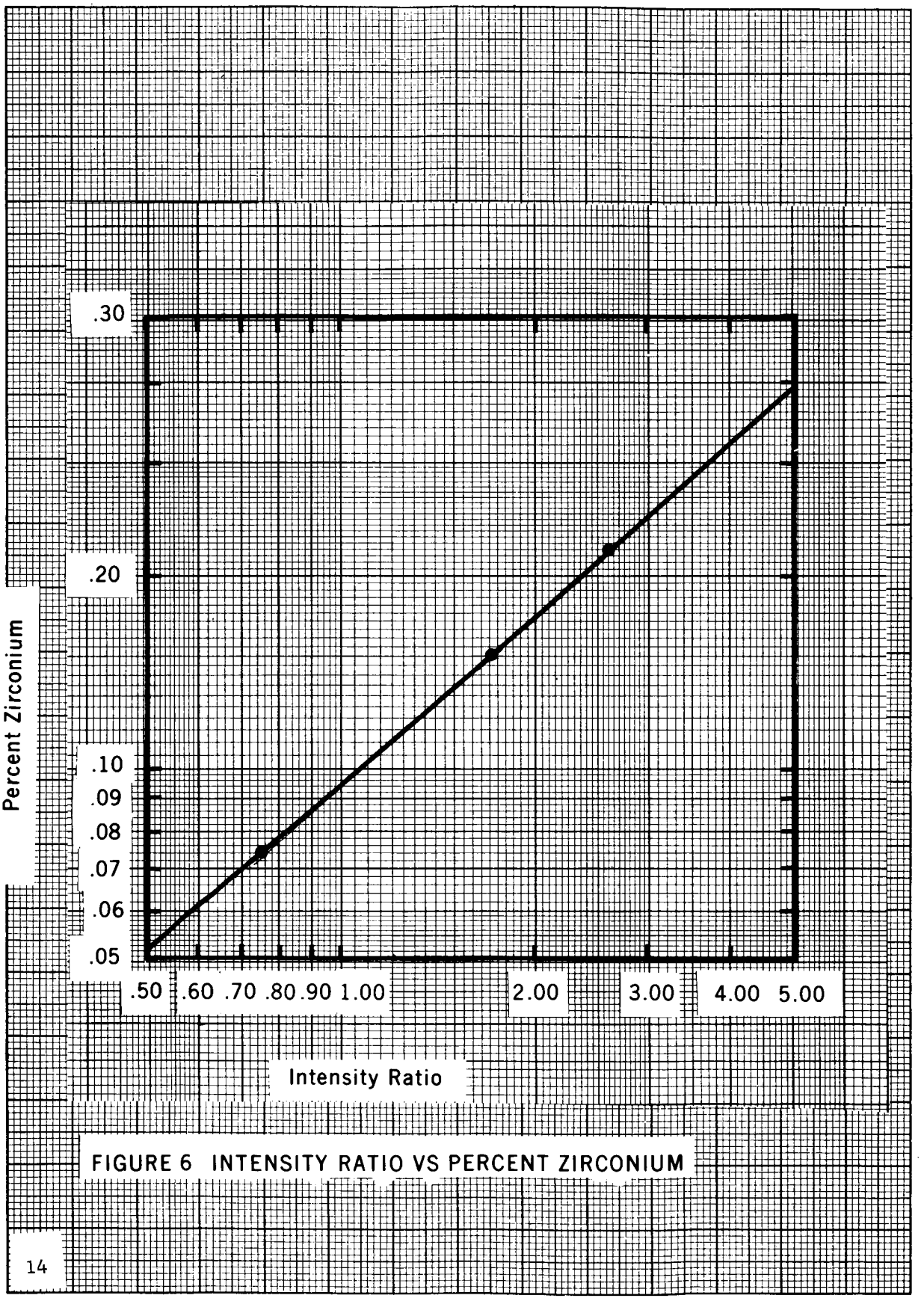

FIGURE 6 INTENSITY RATIO VS PERCENT ZIRCONIUM

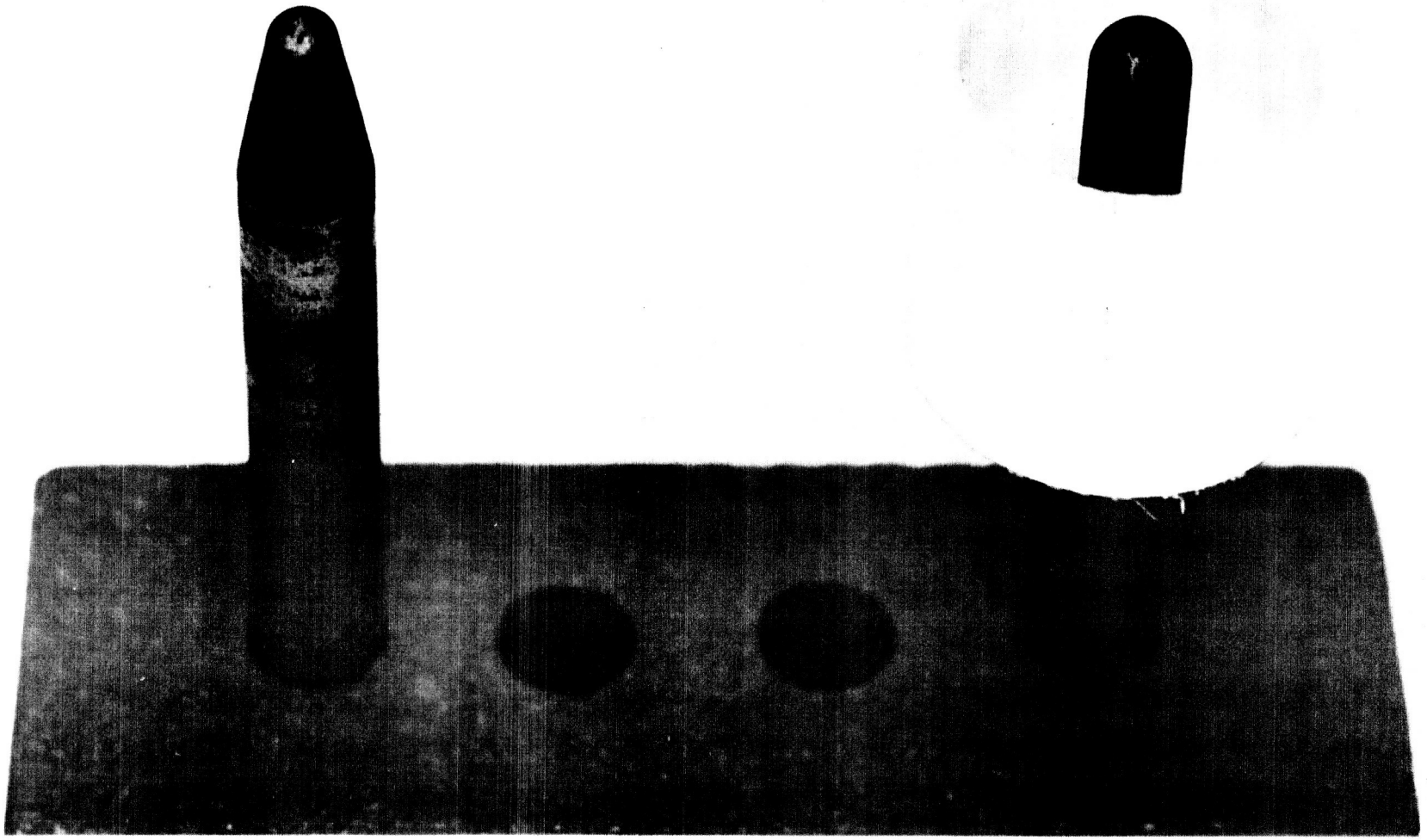

PLATE 1 VACUUM CUP ELECTRODE WITH TEFLON CUP FOR SOLUTION AND COUNTER ELECTRODE

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The information in this report has been reviewed for security classification. Review of any information concerning Department of Defense or Atomic Energy Commission programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.

This document has also been reviewed and approved for technical accuracy.

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